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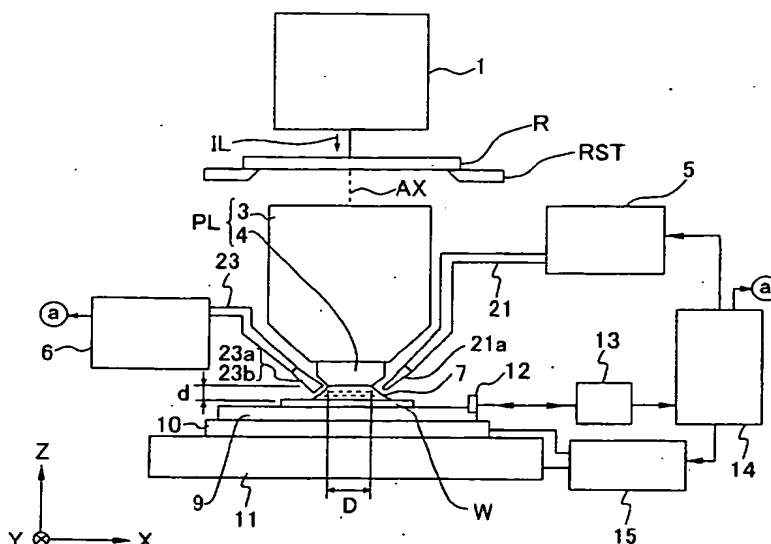
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**Tokyo 100-8831 (JP)**(54) **OPTICAL DEVICE AND PROJECTION EXPOSURE APPARATUS USING SUCH OPTICAL DEVICE**

(57) A liquid immersion exposure apparatus includes a projection optical system (PL) which projects an image of a pattern onto a substrate (W) and a unit (5) which supplies a liquid (7) between an optical element (4) at the end of the projection optical system (PL) and the substrate (W). A corrosion-resistant film com-

posed of an oxide is formed on the surface of the optical element (4) to prevent corrosion by the liquid (7). Consequently, a desired performance of the projection optical system can be secured for a long time even where a full field exposure in the step-and-repeat manner or a scanning exposure in the step-and-scan manner is performed in a liquid-immersion state.

**Fig. 1**

## Description

### TECHNICAL FIELD

[0001] The present invention relates to a projection exposure apparatus which is usable to transfer a mask pattern onto a photosensitive substrate in the lithography step for producing devices including, for example, semiconductor elements, image pickup elements (CCD or the like), liquid crystal display elements, and thin film magnetic heads. In particular, the present invention relates to a projection exposure apparatus based on the use of the liquid immersion method. The present invention also relates to an optical element which is usable for the projection exposure apparatus.

### BACKGROUND ART

[0002] In the production of the semiconductor element or the like, the projection exposure apparatus is used to transfer a pattern image of a reticle as a mask via a projection optical system onto each of shot areas on a wafer (or a glass plate or the like) coated with a resist as a photosensitive substrate. Conventionally, the reduction projection type exposure apparatus based on the step-and-repeat system (stepper) has been used as the projection exposure apparatus in many cases. However, recently, the attention is also attracted to the projection exposure apparatus based on the step-and-scan system in which the exposure is performed by synchronously scanning the reticle and the wafer.

[0003] As for the resolution of the projection optical system carried on the projection exposure apparatus, as the exposure wavelength to be used is shorter, the resolution becomes higher. Further, as the numerical aperture of the projection optical system is larger, the resolution becomes higher. Therefore, the exposure wavelength, which is used for the projection exposure apparatus, is shortened year by year, and the numerical aperture of the projection optical system is increased as well, as the integrated circuit becomes fine and minute. The exposure wavelength, which is dominantly used at present, is 248 nm based on the KrF excimer laser. However, the exposure wavelength of 193 nm based on the ArF excimer laser, which is shorter than the above, is also practically used.

[0004] When the exposure is performed, the depth of focus (DOF) is also important in the same manner as the resolution. The resolution  $R$  and the depth of focus  $\delta$  are represented by the following expressions respectively.

$$R = k1 \cdot \lambda / NA \quad (1)$$

$$\delta = \pm k2 \cdot \lambda / NA^2 \quad (2)$$

[0005] In the expressions,  $\lambda$  represents the exposure wavelength,  $NA$  represents the numerical aperture of the projection optical system, and  $k1$  and  $k2$  represent the process coefficients. According to the expressions (1) and (2), the following fact is appreciated. That is, when the exposure wavelength  $\lambda$  is shortened and the numerical aperture  $NA$  is increased in order to enhance the resolution  $R$ , then the depth of focus  $\delta$  is narrowed. Conventionally, in the projection exposure apparatus, the surface of the wafer is adjusted and matched with the image plane of the projection optical system in the auto-focus manner. For this purpose, it is desirable that the depth of focus  $\delta$  is wide to some extent. Accordingly, those having been suggested as the method for substantially widening the depth of focus include, for example, the phase shift reticle method, the modified illumination method, and the multilayer resist method.

[0006] As described above, in the conventional projection exposure apparatus, the depth of focus is narrowed as the wavelength of the exposure light beam is shortened and the numerical aperture of the projection optical system is increased. In order to respond to the advance of higher integration of the semiconductor integrated circuit, studies have been also made to further shorten the exposure wavelength. However, if such a situation is continued as it is, it is feared that the depth of focus may be too narrowed and the margin may become insufficient during the exposure operation.

[0007] In view of the above, the liquid immersion method has been proposed as a method for substantially shortening the exposure wavelength and deepening the depth of focus. In this method, the space between the lower surface of the projection optical system and the surface of the wafer is filled with a liquid such as water or an organic solvent. The resolution is improved and the depth of focus is magnified about  $n$  times by utilizing the fact that the wavelength of the exposure light beam in the liquid is  $1/n$  time that in the air ( $n$  represents the refractive index of the liquid, which is usually about 1.2 to 1.6).

[0008] If it is intended to apply the liquid immersion method to the projection exposure apparatus based on the step-and-repeat system as it is, the liquid leaks out from the space between the projection optical system and the wafer when the wafer is subjected to the stepping movement to the next shot area after the exposure is completed for one shot area. Therefore, inconveniences arise such that the liquid must be supplied again, and it is difficult to recover the leaked liquid as well. If it is intended to apply the liquid immersion method to the projection exposure apparatus based on the step-and-scan system, it is necessary that the space between the projection optical system and the wafer is filled with the liquid during the period in which the wafer is moved as well, because the exposure is performed while moving the wafer. The projection optical system and the liquid make contact with each other. Therefore, there is such a possibility that the end portion of the projection optical

system, which is in contact with the liquid, may be corroded by the liquid. The objective lens is installed to the end of the projection optical system. If the objective lens is corroded, it is feared that any desired optical performance cannot be obtained.

#### DISCLOSURE OF THE INVENTION

[0009] Taking the foregoing viewpoints into consideration, an object of the present invention is to provide an optical element which is preferably usable for a projection exposure system of an exposure apparatus for performing the liquid immersion exposure. Another object of the present invention is to provide a projection exposure apparatus for the liquid immersion exposure which carries such an optical element.

[0010] According to a first aspect of the present invention, there is provided an optical element usable for a projection optical system which exposes a substrate by projecting a predetermined pattern onto the substrate, the optical element comprising:

a base of the optical element which is installed to an end of the projection optical system on a side of the substrate and through which the exposure is performed in a state that a liquid is maintained between the optical element and the substrate; and a corrosion resistant film which is formed on at least a part of a surface of the base of the optical element to avoid corrosion by the liquid.

[0011] The corrosion resistant film is formed on the surface of the base of the optical element of the present invention. Therefore, even when the liquid immersion exposure is performed, it is possible to avoid, for example, the corrosion, the erosion, and the dissolution which would be otherwise caused by the contact between the optical element and the liquid. Therefore, the desired performance of the projection optical system can be maintained over a long term even when the full field exposure such as those in the step-and-repeat manner or the scanning type exposure such as those in the step-and-scan manner, in which the optical element installed to the end of the projection optical system is exposed to the liquid repeatedly or continuously, is performed in the liquid immersion state.

[0012] According to a second aspect of the present invention, there is provided an exposure apparatus which exposes a substrate by projecting an image of a predetermined pattern onto the substrate through a liquid, the exposure apparatus comprising:

a projection optical system which projects the image of the pattern onto the substrate;  
an optical element which is installed to an end of the projection optical system on a side of the substrate; and  
an apparatus which supplies the liquid to a space

between the optical element and the substrate, wherein:

the optical element includes a base, and a corrosion resistant film which is formed on at least a part of a surface of the base to avoid corrosion of the base.

[0013] The corrosion resistant film is formed on the surface of the base of the optical element installed to the tip of the projection optical system of the exposure apparatus of the present invention. Therefore, even when the liquid immersion exposure is performed, it is possible to avoid, for example, the corrosion, the erosion, and the dissolution which would be otherwise caused by the contact between the optical element and the liquid. Therefore, the desired optical characteristics of the exposure apparatus can be maintained over a long term even when the full field exposure such as those based on the step-and-repeat system or the scanning type exposure such as those based on the step-and-scan system, in which the optical element installed to the end of the projection optical system is exposed to the liquid repeatedly or continuously, is performed in the liquid immersion state. Accordingly, it is possible to realize the exposure in a state in which the wide depth of focus is maintained.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

Fig. 1 shows a schematic arrangement of a projection exposure apparatus according to the present invention.

Fig. 2 shows a positional relationship between an end portion 4A of an optical element 4 of a projection optical system PL shown in Fig. 1 and discharge nozzles and inflow nozzles for the X direction.

Fig. 3 shows a positional relationship between the end portion 4A of the optical element 4 of the projection optical system PL shown in Fig. 1 and discharge nozzles and inflow nozzles for supplying and recovering the liquid in the Y direction.

Fig. 4 shows a magnified view illustrating major parts to depict a situation of the supply and the recovery of the liquid 7 with respect to the space between the optical element 4 and a wafer W shown in Fig. 1.

Fig. 5 shows a front view illustrating, for example, a lower end portion of a projection optical system PLA of a projection exposure apparatus, a liquid supply unit 5, and a liquid recovery unit 6 to be used in a second embodiment of the present invention.

Fig. 6 shows a positional relationship between an end portion 32A of an optical element 32 of the projection optical system PLA shown in Fig. 5 and dis-

charge nozzles and inflow nozzles for the X direction.

Fig. 7 shows a positional relationship between the end portion 32A of the optical element 32 of the projection optical system PLA shown in Fig. 5 and discharge nozzles and inflow nozzles for supplying and recovering the liquid in the Y direction.

Fig. 8 shows a schematic arrangement of the optical element of the present invention.

Fig. 9 shows a relationship between the angle of incidence and the reflectance of the ArF excimer laser (wavelength: 193 nm) when an optical element is constructed by only fluorite.

Fig. 10 shows a relationship between the angle of incidence and the reflectance of the ArF excimer laser (wavelength: 193 nm) when an optical element 105 has respective layers formed on a fluorite base.

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0015] An explanation will be made below with reference to the drawings about embodiments of the optical element of the present invention and the projection exposure apparatus based on the use of the optical element. However, the present invention is not limited thereto.

[0016] At first, the optical element of the present invention will be explained with reference to Figs. 8 to 10. Fig. 8 shows a cross-sectional structure of an optical element 105 of the present invention. The optical element 105 includes an SiO<sub>2</sub> layer 102, an Al<sub>2</sub>O<sub>3</sub> layer 103, and an SiO<sub>2</sub> layer 104 which are stacked in this order on a fluorite (CaF<sub>2</sub>) base 101. These layers or the an SiO<sub>2</sub> layer disposed on the outermost surface functions as the corrosion resistant film (erosion resistant film). The fluorite base 101 is formed to be lens-shaped, and it has a thickness of 20 mm. The SiO<sub>2</sub> layer 102, the Al<sub>2</sub>O<sub>3</sub> layer 103, and the SiO<sub>2</sub> layer 104 are formed so that the optical thicknesses are 0.37λ, 0.05λ, and 0.37λ with respect to the designed main wavelength λ (for example, λ = 193 nm) respectively. A known sputtering method was used for each of the layers so that the dense film was successfully formed. The film formation method is not limited to the sputtering method. It is also allowable to use, for example, the ion beam assist method, the ion plating method, and the heating vapor deposition method provided that the dense film can be formed. The corrosion resistant films as described above may be provided on the both sides of the base 101 respectively. Alternatively, the corrosion resistant film as described above may be provided at only the portion of the base 101 to be irradiated with the light beam.

#### Investigation of Reflectance Characteristics

[0017] The reflectance characteristics were investigated in relation to the angle of incidence of the light

beam into the optical element 105 obtained as described above. In order to make comparison with the optical element 105 (hereinafter referred to as "optical element A"), a fluorite base stacked with neither the SiO<sub>2</sub> layer nor the Al<sub>2</sub>O<sub>3</sub> layer, i.e., an optical element composed of only the fluorite base (hereinafter referred to as "optical element B") was prepared. The ArF excimer laser beam having a wavelength of 193 nm, which was used as the exposure light beam for the exposure apparatus, was radiated onto the optical element A and the optical element B respectively while changing the angle of incidence to measure the reflectances. Obtained results are shown in Figs. 9 and 10. The reflected light beams were measured for the S-polarized light and the P-polarized light which were orthogonal to one another.

[0018] Fig. 9 shows a graph illustrating the reflectance characteristic of the optical element B with respect to the angle of incidence. As shown in Fig. 9, the average reflectance of the S-polarized light and the P-polarized light in relation to the optical element B was not more than about 0.04 % in all regions ranging to the maximum angle of incidence of 40 degrees in which the optical element was to be used.

[0019] Fig. 10 shows a graph illustrating the reflectance characteristic of the optical element A with respect to the angle of incidence. As shown in Fig. 10, the average reflectance of the S-polarized light and the P-polarized light was not more than about 0.04 % in all regions ranging to the maximum angle of incidence of 40 degrees in which the optical element was to be used.

[0020] That is, the optical element A exhibits the low values of the average reflectance of the S-polarized light and the P-polarized light in all regions of the angle of incidence assumed for the use as the optical element, in the same manner as the optical element B composed of only fluorite. It is appreciated that the optical element A can be carried at the end portion of the projection optical system of the projection exposure apparatus in place of the optical element B.

#### Evaluation of Corrosion Resistance

[0021] Next, an acceleration test was carried out for the corrosion resistance by immersing the optical element A and the optical element B in pure water at 70 °C for 3 hours respectively. The surface roughnesses of the optical elements were measured by using an AFM (atomic force microscope) and a contact type roughness meter. It is assumed that the immersion in pure water at 70 °C for 3 hours corresponds to the immersion in pure water at room temperature for about 10 days.

[0022] The surface roughness, which was obtained before immersing the optical element B composed of only fluorite in pure water, was 3 angstrom RMS. The surface roughness, which was obtained after immersing the optical element B in pure water, was about 3,000 angstrom RMS. Therefore, it is understood that the op-

tical element B was corroded to have the about 1,000 times surface roughness. When the surface roughness of the surface of the optical element is 3,000 angstrom RMS as described above, the scattering of light is caused to a large extent. Therefore, the transmittance of the optical element is lowered, and any deviation arises from the designed optical path. Therefore, it is impossible to exhibit any intended desired optical performance.

[0023] On the other hand, the surface roughness of the optical element A according to the present invention before being immersed in pure water was 11 angstrom RMS. The surface roughness of the optical element after being immersed in pure water was 14 angstrom RMS. Therefore, it is appreciated that the surface roughness of the optical element is scarcely changed before and after being immersed in pure water. Therefore, the optical element A can maintain the desired optical performance after being immersed in pure water, i.e., even when the liquid immersion exposure is performed, probably for the following reason. That is, it is considered that the oxide coating film, which is formed on the surface of the fluorite base, prevents the fluorite base from corrosion, because the oxide coating film has the corrosion resistance against pure water.

[0024] In the optical element A of this embodiment, the three-layered multilayer film composed of the oxides is formed on the fluorite base. However, it has been revealed that the same or equivalent effect is obtained even when a single layer film of, for example,  $\text{SiO}_2$  (optical film thickness:  $0.55\lambda$ ) or  $\text{Al}_2\text{O}_3$  is formed. The film thickness of the multilayer film or the single layer film having the corrosion resistance is not specifically limited. However, it is desirable that the film thickness is 50 angstroms to 2,000 angstroms in view of the fact that the covering performance of the film on the surface of the fluorite base is secured, and the angular reflection-preventive performance is secured.

[0025] In this embodiment, the  $\text{SiO}_2$  layer and the  $\text{Al}_2\text{O}_3$  layer are formed on the fluorite base. However, in place of these layers or together with these layers, a layer or layers of fluoride or fluorides such as  $\text{YF}_3$ ,  $\text{MgF}_2$ , and  $\text{LaF}_3$  may be formed singly or in combination.

[0026] Next, an explanation will be made with reference to Figs. 1 to 4 about a second embodiment illustrative of a projection exposure apparatus to which the optical element of the embodiment described above is applied. The projection exposure apparatus of this embodiment is a projection exposure apparatus based on the step-and-repeat system for performing the full field exposure for the shot area on the substrate.

[0027] Fig. 1 shows a schematic arrangement of the projection exposure apparatus of this embodiment. With reference to Fig. 1, the exposure light beam IL, which is composed of an ultraviolet pulse light beam having a wavelength of 193 nm, is radiated from an illumination optical system 1 including, for example, an ArF excimer laser light source as an exposure light source, an optical

integrator (homogenizer), a field diaphragm, and a condenser lens.

The exposure light beam IL illuminates a pattern provided on a reticle R. The pattern of the reticle R is subjected to the reduction projection onto an exposure area on a wafer W coated with a photoresist at a predetermined projection magnification  $\beta$  ( $\beta$  is, for example,  $1/4$  or  $1/5$ ) via a projection optical system PL which is telecentric on the both sides (or on one side of the wafer W). Those usable as the exposure light beam IL also include, for example, the KrF excimer laser beam (wavelength: 248 nm), the  $\text{F}_2$  laser beam (wavelength: 157 nm), and the i-ray (wavelength: 365 nm) of the mercury lamp.

[0028] In the following description, it is assumed that the Z axis extends in the direction parallel to the optical axis AX of the projection optical system PL, the Y axis extends in the direction perpendicular to the sheet surface of Fig. 1 in the plane perpendicular to the Z axis, and the X axis extends in parallel to the sheet surface of Fig. 1.

[0029] The reticle R is held on a reticle stage RST. A mechanism, which finely moves the reticle R in the X direction, the Y direction, and the rotational direction, is incorporated in the reticle stage RST. The two-dimensional position and the angle of rotation of the reticle stage RST are measured in real-time by a laser interferometer (not shown). A main control system 14 positions the reticle R on the basis of the value measured by the laser interferometer.

[0030] On the other hand, the wafer W is fixed on a Z stage 9 which controls the focus position (position in the Z direction) and the angle of inclination of the wafer W by the aid of a wafer holder (not shown). The Z stage 9 is fixed on an XY stage 10 which is movable along the XY plane that is substantially parallel to the image plane of the projection optical system PL. The XY stage 10 is placed on a base 11. The Z stage 9 controls the focus position (position in the Z direction) and the angle of inclination of the wafer W to adjust and match the surface of the wafer W with respect to the image plane of the projection optical system PL in the auto-focus manner and the auto-leveling manner. The XY stage 10 positions the wafer W in the X direction and the Y direction. The two-dimensional position and the angle of rotation of the Z stage 9 (wafer W) are measured in real-time as a position of a movement mirror 12 by a laser interferometer 13. The control information is fed from the main control system 14 to a wafer stage-driving system 15 on the basis of the measured result. The wafer stage-driving system 15 controls the operation of the Z stage 9 and the XY stage 10 on the basis of the control information. During the exposure, the operation, in which each of the shot areas on the wafer W is successively subjected to the stepping movement to the exposure position to perform the exposure with the pattern image of the reticle R, is repeated in the step-and-repeat manner.

[0031] The liquid immersion method is applied to the projection exposure apparatus of this embodiment in or-

der that that the resolution is improved by substantially shortening the exposure wavelength, and the depth of focus is substantially widened. Therefore, the space between the surface of the wafer W and the tip surface (lower surface) of the projection optical system PL is filled with a predetermined liquid 7 at least during the period in which the pattern image of the reticle R is transferred onto the wafer W. The projection optical system PL has a plurality of optical elements which include the optical element 4 as produced in the embodiment described above, and a barrel 3 which accommodates the optical elements. The optical element 4 is installed so that the optical element 4 is exposed at the end (lower end) of the barrel on the side of the wafer (see Figs. 4 and 5). When the optical element 4 is installed as described above, only the optical element 4 makes contact with the liquid 7. Accordingly, the barrel 3, which is composed of metal, is prevented from the corrosion or the like. In this embodiment, pure water is used as the liquid 7. Pure water is advantageous in that pure water is available in a large amount with ease, for example, in the semiconductor production factory, and pure water exerts no harmful influence, for example, on the optical lens and the photoresist on the wafer. Further, pure water exerts no harmful influence on the environment, and the content of impurity is extremely low. Therefore, it is also expected to obtain the function to wash the surface of the wafer.

**[0032]** It is approved that the refractive index  $n$  of pure water (water) with respect to the exposure light beam having a wavelength of about 200 nm is approximately in an extent of 1.44 to 1.47. The wavelength of the ArF excimer laser beam of 193 nm is shortened on the wafer W by  $1/n$ , i.e., to about 131 to 134 nm, and a high resolution is obtained. Further, the depth of focus is magnified about  $n$  times, i.e., about 1.44 to 1.47 times as compared with the value obtained in the air. Therefore, when it is enough to secure an approximately equivalent depth of focus as compared with the case of the use in the air, it is possible to further increase the numerical aperture of the projection optical system PL. Also in this viewpoint, the resolution is improved.

**[0033]** The liquid 7 is supplied in a temperature-controlled state onto the wafer W by the aid of predetermined discharge nozzles or the like by a liquid supply unit 5 including, for example, a tank for accommodating the liquid, a pressurizing pump, and a temperature control unit. The liquid 7, which has been supplied onto the wafer W, is recovered by the aid of predetermined inflow nozzles or the like by a liquid recovery unit 6 including, for example, a tank for accommodating the liquid, and a suction pump. The temperature of the liquid 7 is set, for example, to be approximately equivalent to the temperature of a chamber in which the projection exposure apparatus of this embodiment is accommodated. The projection exposure apparatus of this embodiment is arranged with a discharge nozzle 21a having a thin tip section and two inflow nozzles 23a, 23b having wide tip sec-

tions so that the end portion of the optical element 4 of the projection optical system PL is interposed in the X direction (see Fig. 2). The discharge nozzle 21a is connected to the liquid supply unit 5 via a supply tube 21, and the inflow nozzles 23a, 23b are connected to the liquid recovery unit 6 via a recovery tube 23. Further, another set of discharge and recovery nozzles are arranged at positions obtained by rotating the positions of the set of the discharge nozzle 21a and the inflow nozzles 23a, 23b by substantially  $180^\circ$  about the center of the end portion of the optical element 4, and two sets of discharge and recovery nozzles are also arranged so that the end portion of the optical element 4 is interposed in the Y direction (see Figs. 2 and 3).

**[0034]** Fig. 2 shows a positional relationship in relation to the end portion 4A of the optical element 4 of the projection optical system PL shown in Fig. 1, the wafer W, and the two sets of the discharge nozzles and the inflow nozzles to interpose the end portion 4A in the X direction. With reference to Fig. 2, the discharge nozzle 21a is arranged on the side in the +X direction with respect to the end portion 4A, and the inflow nozzles 23a, 23b are arranged on the side in the -X direction. The inflow nozzles 23a, 23b are arranged in a sector-shaped open form with respect to the axis which passes through the center of the end portion 4A and which is parallel to the X axis. Another set of the discharge nozzle 22a and the inflow nozzles 24a, 24b are arranged at the positions obtained by rotating the positions of the set of the discharge nozzle 21a and the inflow nozzles 23a, 23b by substantially  $180^\circ$  about the center of the end portion 4A. The discharge nozzle 22a is connected to the liquid supply unit 5 via a supply tube 22, and the inflow nozzles 24a, 24b are connected to the liquid recovery unit 6 via a recovery tube 24.

**[0035]** Fig. 3 shows a positional relationship in relation to the end portion 4A of the optical element 4 of the projection optical system PL shown in Fig. 1 and the two sets of the discharge nozzles and the inflow nozzles to interpose the end portion 4A in the Y direction. With reference to Fig. 3, the discharge nozzle 27a is arranged on the side in the +Y direction with respect to the end portion 4A, and the inflow nozzles 29a, 29b are arranged on the side in the -Y direction. The discharge nozzle 27a is connected to the liquid supply unit 5 via a supply tube 27, and the inflow nozzles 29a, 29b are connected to the liquid recovery unit 6 via a recovery tube 29. Another set of the discharge nozzle 28a and the inflow nozzles 30a, 30b are arranged at the positions obtained by rotating the positions of the set of the discharge nozzle 27a and the inflow nozzles 29a, 29b by substantially  $180^\circ$  about the center of the end portion 4A. The discharge nozzle 28a is connected to the liquid supply unit 5 via a supply tube 28, and the inflow nozzles 30a, 30b are connected to the liquid recovery unit 6 via a recovery tube 30. The liquid supply unit 5 supplies the temperature-controlled liquid to the space between the wafer W and the end portion 4A of the optical element 4 via at

least one of the supply tubes 21, 22, 27, 28. The liquid recovery unit 6 recovers the liquid supplied onto the wafer W via at least one of the recovery tubes 23, 24, 29, 30.

[0036] Next, an explanation will be made about a supply method and a recovery method for the liquid 7.

[0037] With reference to Fig. 2, when the wafer W is subjected to the stepping movement in the direction of the arrow 25A indicated by the solid line (-X direction), the liquid supply unit 5 supplies the liquid 7 to the space between the wafer W and the end portion 4A of the optical element 4 via the supply tube 21 and the discharge nozzle 21a. The liquid recovery unit 6 recovers the liquid 7 from the surface of the wafer W via the recovery nozzle 23 and the inflow nozzles 23a, 23b. In this situation, the liquid 7 flows in the direction of the arrow 25B (-X direction) on the wafer W. The space between the wafer W and the optical element 4 is filled with the liquid 7 in a stable state.

[0038] On the other hand, when the wafer W is subjected to the stepping movement in the direction of the arrow 26A indicated by the two-dot chain line (+X direction), then the liquid supply unit 5 supplies the liquid 7 to the space between the wafer W and the end portion 4A of the optical element 4 by using the supply tube 22 and the discharge nozzle 22a, and the liquid recovery unit 6 recovers the liquid 7 by using the recovery tube 24 and the inflow nozzles 24a, 24b. In this situation, the liquid 7 flows in the direction of the arrow 26B (+X direction) on the wafer W. The space between the wafer W and the optical element 4 is filled with the liquid 7 in a stable state. As described above, the projection exposure apparatus of this embodiment is provided with the two sets of the discharge nozzles and the inflow nozzles which are inverted to one another in the X direction. Therefore, even when the wafer W is moved in any one of the +X direction and the -X direction, the space between the wafer W and the optical element 4 can be filled with the liquid 7 in the stable state.

[0039] In the exposure apparatus of this embodiment, the liquid 7 flows on the wafer W. Therefore, even when any foreign matter is adhered onto the wafer W, the foreign matter can be washed out with the liquid 7. The liquid 7 is adjusted to have a predetermined temperature by the liquid supply unit 5. Therefore, the surface of the wafer W is temperature-adjusted, and it is possible to avoid the decrease in the overlay accuracy or the like which would be otherwise caused by the thermal expansion of the wafer brought about by the heat generated during the exposure. Therefore, even when a certain period of time is required from the alignment to the exposure as in the EGA (enhanced global alignment) system, it is possible to avoid the decrease in the overlay accuracy which would be otherwise caused by the thermal expansion of the wafer possibly brought about during such a period. In the projection exposure apparatus of this embodiment, the liquid 7 flows in the same direction as the direction in which the wafer W is moved. There-

fore, the liquid, which has absorbed the foreign matter and the heat, can be recovered without allowing the liquid to stay on the exposure area disposed just under the end portion 4A of the optical element 4.

[0040] When the wafer W is subjected to the stepping movement in the Y direction, the liquid 7 is supplied and recovered in the Y direction. That is, when the wafer is subjected to the stepping movement in the direction of the arrow 31A (-Y direction) indicated by the solid line in Fig. 3, then the liquid supply unit 5 supplies the liquid via the supply tube 27 and the discharge nozzle 27a, and the liquid recovery unit 6 recovers the liquid by using the recovery tube 29 and the inflow nozzles 29a, 29b. Accordingly, the liquid flows in the direction of the arrow 31B (-Y direction) on the exposure area disposed just under the end portion 4A of the optical element 4. When the wafer is subjected to the stepping movement in the direction of the arrow 33A (+Y direction) indicated by the two-dot chain line, the liquid is supplied and recovered by using the supply tube 28, the discharge nozzle 28a, the recovery tube 30, and the inflow nozzles 30a, 30b. Accordingly, the liquid flows in the direction of the arrow 33B (+Y direction) on the exposure area disposed just under the end portion 4A. Therefore, even when the wafer W is moved in any one of the +Y direction and the -Y direction, the space between the wafer W and the end portion 4A of the optical element 4 can be filled with the liquid 7 in a stable state, in the same manner as in the case in which the wafer W is moved in the X direction.

[0041] There is no limitation to the provision of the nozzles for supplying and recovering the liquid 7 in the X direction and/or the Y direction. It is also allowable to provide nozzles for supplying and recovering the liquid 7, for example, in oblique directions.

[0042] Next, an explanation will be made about a method for controlling the supply amount and the recovery amount of the liquid 7. Fig. 4 shows a situation in which the liquid is supplied to and recovered from the space between the wafer W and the optical element 4 of the projection optical system PL. With reference to Fig. 4, the wafer W is moved in the direction of the arrow 25A (-X direction). The liquid 7, which is supplied by the discharge nozzle 21a, flows in the direction of the arrow 25B (-X direction), and the liquid 7 is recovered by the inflow nozzles 23a, 23b. In order to maintain a constant amount of the liquid 7 existing between the optical element 4 and the wafer W even during the movement of the wafer W, the supply amount  $V_i$  ( $\text{m}^3/\text{s}$ ) of the liquid 7 is equal to the recovery amount  $V_o$  ( $\text{m}^3/\text{s}$ ) thereof in this embodiment. Further, the supply amount  $V_i$  and the recovery amount  $V_o$  of the liquid 7 are adjusted to be proportional to the movement velocity  $v$  of the XY stage (wafer W). That is, the main control system 14 determines the supply amount  $V_i$  and the recovery amount  $V_o$  of the liquid 7 in accordance with the following expression.

$$V_i = V_o = D \cdot v \cdot d \quad (3)$$

[0043] In this expression, as shown in Fig. 1, D represents the diameter (m) of the end portion of the optical element 4, v represents the movement velocity (m/s) of the XY stage, and d represents the working distance (distance between the lowermost surface of the optical element 4 and the surface of the wafer W) (m) of the projection optical system PL. The velocity v, at which the XY stage 10 is subjected to the stepping movement, is set by the main control system 14. D and d are previously inputted into (stored in) the main control system 14. Therefore, when the supply amount  $V_i$  of the liquid 7 and the recovery amount  $V_o$  thereof are adjusted on the basis of the expression (3), a state is given, in which the space between the wafer W and the optical element 4 shown in Fig. 4 is always filled with the liquid 7.

[0044] It is desirable that the working distance d of the projection optical system PL is made as narrow as possible in order that the liquid 7 stably exists between the projection optical system PL and the wafer W. However, if the working distance d is too small, it is feared that the surface of the wafer W may make contact with the optical element 4. Therefore, it is necessary to provide a margin to some extent. Accordingly, the working distance d is set to be, for example, about 2 mm.

[0045] Next, a third embodiment of the present invention will be explained with reference to Figs. 5 to 7. In this embodiment, the optical element of the embodiment described above is applied to a projection exposure apparatus based on the step-and-scan system.

[0046] Fig. 5 shows a front view illustrating, for example, a lower portion of a projection optical system PLA of the projection exposure apparatus of this embodiment, a liquid supply unit 5, and a liquid recovery unit 6. The same or equivalent constitutive components as those shown in Fig. 4 are designated by the same reference numerals. With reference to Fig. 5, an optical element 32, which is disposed at a lowermost end of a barrel 3A of the projection optical system PLA, has an end portion 32A which is formed so that the end portion has a rectangular shape which is long in the Y direction (non-scanning direction) and which has a necessary portion for the scanning exposure. The optical element 32 is such an optical element that a corrosion resistant film, which is equivalent to that of the optical element produced in the first embodiment, is provided on a fluoride base. During the scanning exposure, a part of a pattern image of the reticle is projected onto a rectangular exposure area disposed just under the end portion 32A. The reticle (not shown) is moved at a velocity V in the -X direction (or in the +X direction) with respect to the projection optical system PLA, in synchronization with which the wafer W is moved at a velocity  $\beta \cdot V$  ( $\beta$  represents the projection magnification) in the +X direction (or in the -X direction) by the aid of the XY stage 10. After the exposure is completed for one shot area, the

next shot area is moved to the scanning start position in accordance with the stepping of the wafer W. In the following procedure, the exposure is successively performed for respective shot areas in the step-and-scan manner.

[0047] The liquid immersion method is also applied in this embodiment, and thus the space between the optical element 32 and the surface of the wafer W is filled with the liquid 7 during the scanning exposure. The liquid 7 is supplied and recovered by using the liquid supply unit 5 and the liquid recovery unit 6 respectively in the same manner as in the second embodiment.

[0048] Fig. 6 shows a positional relationship between the end portion 32A of the optical element 32 of the projection optical system PLA and the discharge nozzles and the inflow nozzles for supplying and recovering the liquid 7 in the X direction. With reference to Fig. 6, the end portion 32A of the optical element 32 has a rectangular shape which is long in the Y direction. The three discharge nozzles 21a to 21c are arranged on the side in the +X direction, and the two inflow nozzles 23a, 23b are arranged on the side in the -X direction so that the end portion 32A of the optical element 32 of the projection optical system PLA is interposed in the X direction.

[0049] The discharge nozzles 21a to 21c are connected to the liquid supply unit 5 via a supply tube 21, and the inflow nozzles 23a, 23b are connected to the liquid recovery unit 6 via a recovery tube 23. The discharge nozzles 22a to 22c and the recovery nozzles 24a, 24b are arranged at positions obtained by rotating the positions of the discharge nozzles 21a to 21c and the recovery nozzles 23a, 23b by substantially 180° about the center of the end portion 32A. The discharge nozzles 21a to 21c and the inflow nozzles 24a, 24b are arranged alternately in the Y direction, and the discharge nozzles 22a to 22c and the inflow nozzles 23a, 23b are arranged alternately in the Y direction. The discharge nozzles 22a to 22c are connected to the liquid supply unit 5 via a supply tube 22, and the inflow nozzles 24a, 24b are connected to the liquid recovery unit 6 via a recovery tube 24.

[0050] When the wafer W is moved in the scanning direction (-X direction) indicated by the solid line arrow to perform the scanning exposure, the liquid 7 is supplied and recovered by the liquid supply unit 5 and the liquid recovery unit 6 by using the supply tube 21, the discharge nozzles 21a to 21c, the recovery tube 23, and the inflow nozzles 23a, 23b. The liquid 7 is allowed to flow in the -X direction so that the space between the optical element 32 and the wafer W is filled therewith. When the wafer W is moved in the direction (+X direction) indicated by the two-dot chain line arrow to perform the scanning exposure, the liquid 7 is supplied and recovered by using the supply tube 22, the discharge nozzles 22a to 22c, the recovery tube 24, and the inflow nozzles 24a, 24b. The liquid 7 is allowed to flow in the +X direction so that the space between the optical element 32 and the wafer W is filled therewith. When the



direction, in which the liquid 7 is allowed to flow, is switched depending on the scanning direction, the space between the wafer W and the end portion 32A of the optical element 32 can be filled with the liquid 7, even when the wafer W is subjected to the scanning exposure in any one of the +X direction and the -X direction. Accordingly, the exposure can be performed at a high resolution and a wide depth of focus.

[0051] The supply amount  $V_i$  ( $\text{m}^3/\text{s}$ ) of the liquid 7 and the recovery amount  $V_o$  ( $\text{m}^3/\text{s}$ ) thereof are determined in accordance with the following expression.

$$V_i = V_o = \text{DSY} \cdot v \cdot d \quad (4)$$

[0052] In this expression, DSY represents the length (m) of the end portion 32A of the optical element 32 in the X direction. Accordingly, the space between the optical element 32 and the wafer W can be filled with the liquid 7 in a stable state even during the scanning exposure.

[0053] The number and the shapes of the nozzles are not specifically limited. For example, the liquid 7 may be supplied and recovered by using two pairs of nozzles for the long side of the end portion 32A. In this case, the discharge nozzles and the inflow nozzles may be arranged while being aligned vertically in order that the liquid can be supplied and recovered in any one of the +X direction and the -X direction.

[0054] When the wafer W is subjected to the stepping movement in the Y direction, the liquid 7 is supplied and recovered in the Y direction in the same manner as in the second embodiment.

[0055] Fig. 7 shows a positional relationship between the end portion 32A of the optical element 32 of the projection optical system PLA and the discharge nozzles and the inflow nozzles for the Y direction. With reference to Fig. 7, when the wafer is subjected to the stepping movement in the non-scanning direction (-Y direction) perpendicular to the scanning direction, the liquid 7 is supplied and recovered by using the discharge nozzle 27a and the inflow nozzles 29a, 29b arranged in the Y direction. When the wafer is subjected to the stepping movement in the +Y direction, the liquid 7 is supplied and recovered by using the discharge nozzle 28a and the inflow nozzles 30a, 30b arranged in the Y direction. The supply amount  $V_i$  ( $\text{m}^3/\text{s}$ ) of the liquid 7 and the recovery amount  $V_o$  ( $\text{m}^3/\text{s}$ ) thereof are determined in accordance with the following expression.

$$V_i = V_o = \text{DSX} \cdot v \cdot d \quad (5)$$

[0056] In this expression, DSX represents the length (m) of the end portion 32A of the optical element 32 in the Y direction. The space between the optical element 32 and the wafer W can be continuously filled with the liquid 7 by adjusting the supply amount of the liquid 7

depending on the movement velocity  $v$  of the wafer W when the stepping movement is performed in the Y direction as well, in the same manner as in the second embodiment.

[0057] As described above, when the wafer W is moved, the liquid is allowed to flow in the direction corresponding to the direction of the movement. Accordingly, the space between the wafer W and the end portion of the projection optical system PL can be continuously filled with the liquid 7.

[0058] The liquid, which is usable as the liquid 7 in the embodiments described above, is not specifically limited to pure water. It is possible to use liquids (for example, cedar oil) which have the transmittance with respect to the exposure light beam, which have the refractive index as high as possible, and which are stable against the photoresist coated to the surface of the wafer and the projection optical system.

[0059] It is a matter of course that the present invention is not limited to the embodiments described above, which may be embodied in other various forms without deviating from the gist or essential characteristics of the present invention.

[0060] The base of the optical element of the present invention is lens-shaped. However, there is no limitation thereto. It is also allowable to use those each of which is formed as a film on a fluorite plate-shaped base as a cover glass to be disposed between the liquid and the conventional fluorite lens.

## INDUSTRIAL APPLICABILITY

[0061] According to the projection exposure apparatus of the present invention, the end portion of the projection optical system is not corroded by the liquid. Therefore, the operation of the apparatus is not stopped in order to exchange the corroded optical element. Accordingly, it is possible to efficiently produce final products having fine patterns. Further, the optical characteristics of the optical element of the present invention are stable, because the optical element is not corroded. When the projection exposure apparatus, which carries the optical element of the present invention, is used, it is possible to produce final products having stable qualities.

## Claims

1. An optical element usable for a projection optical system which exposes a substrate by projecting a predetermined pattern onto the substrate, the optical element comprising:

a base of the optical element which is installed to an end of the projection optical system on a side of the substrate and through which the exposure is performed in a state that a liquid is

maintained between the optical element and the substrate; and  
a corrosion resistant film which is formed on at least a part of a surface of the base of the optical element to avoid corrosion by the liquid. 5

2. The optical element according to claim 1, wherein the corrosion resistant film is an oxide film.
3. The optical element according to claim 2, wherein the oxide film is at least one of a silicon oxide film and an aluminum oxide film. 10
4. The optical element according to claim 1, wherein the base of the optical element is fluorite. 15
5. The optical element according to claim 1, wherein a light beam, which is used for the exposure, is an ArF laser beam. 20
6. The optical element according to claim 1, wherein the liquid is pure water.
7. An exposure apparatus which exposes a substrate by projecting an image of a predetermined pattern onto the substrate through a liquid, the exposure apparatus comprising: 25
  - a projection optical system which projects the image of the pattern onto the substrate; 30
  - an optical element which is installed to an end of the projection optical system on a side of the substrate; and
  - an apparatus which supplies the liquid to a space between the optical element and the substrate, wherein: 35
    - the optical element includes a base, and a corrosion resistant film which is formed on at least a part of a surface of the base in order to avoid corrosion of the base. 40
8. The exposure apparatus according to claim 7, wherein the corrosion resistant film is an oxide film. 45
9. The exposure apparatus according to claim 8, wherein the corrosion resistant film is a multilayer oxide film.
10. The exposure apparatus according to claim 8, wherein the oxide film is at least one of a silicon oxide film and an aluminum oxide film. 50
11. The exposure apparatus according to claim 7, wherein the base of the optical element is fluorite. 55
12. The exposure apparatus according to claim 11, wherein a light beam, which is used for the expo-

sure, is an ArF laser beam.

13. The exposure apparatus according to claim 7, wherein the liquid is pure water.

Fig. 1

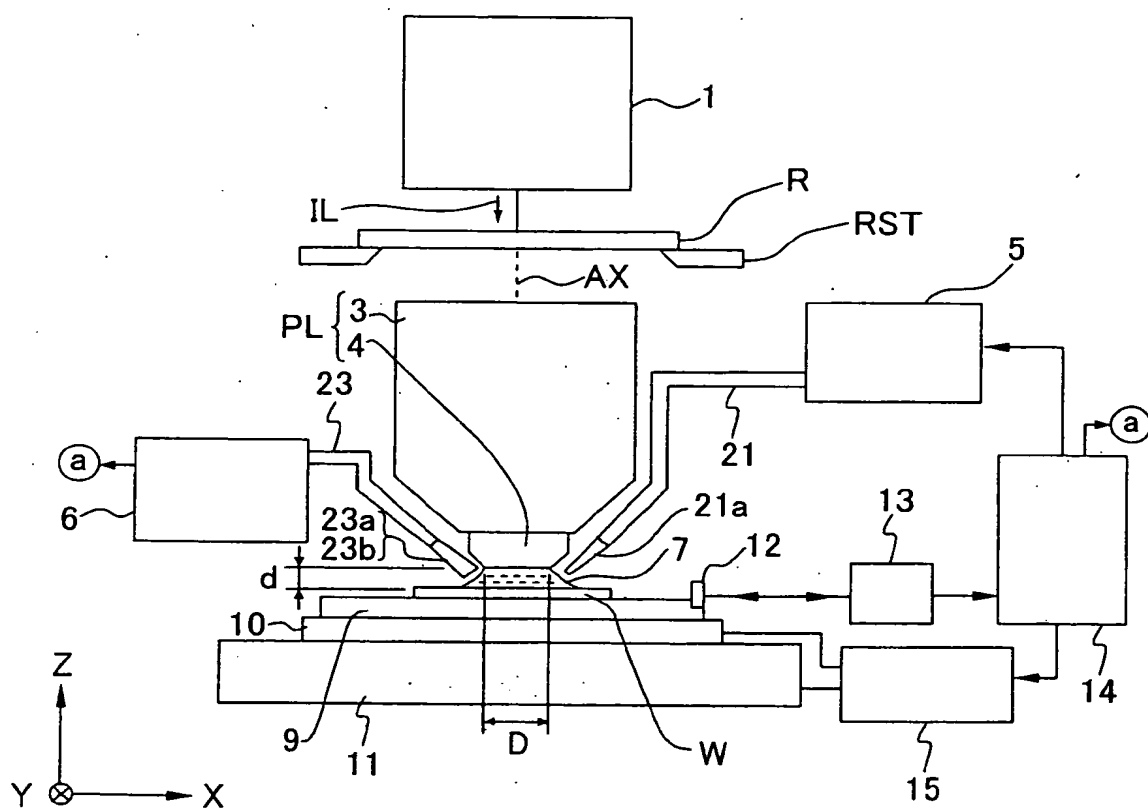


Fig. 2

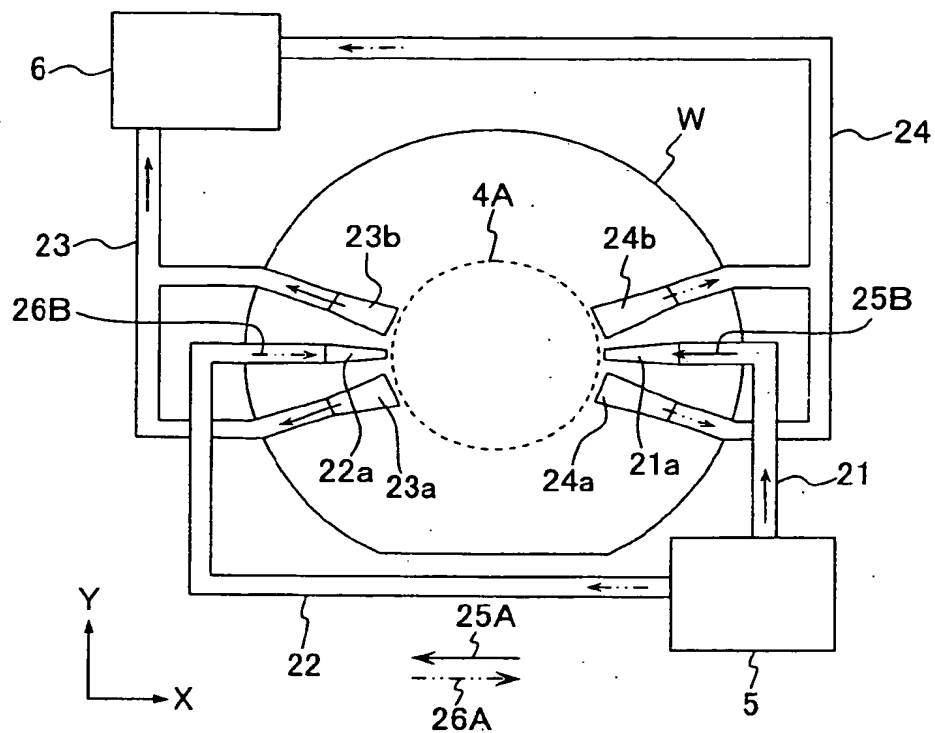


Fig. 3

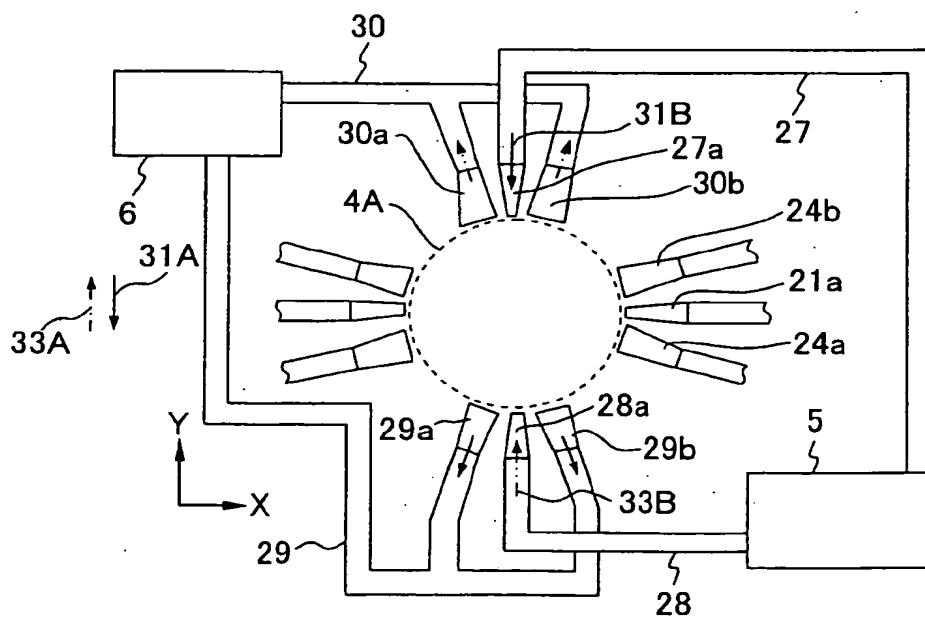


Fig. 4

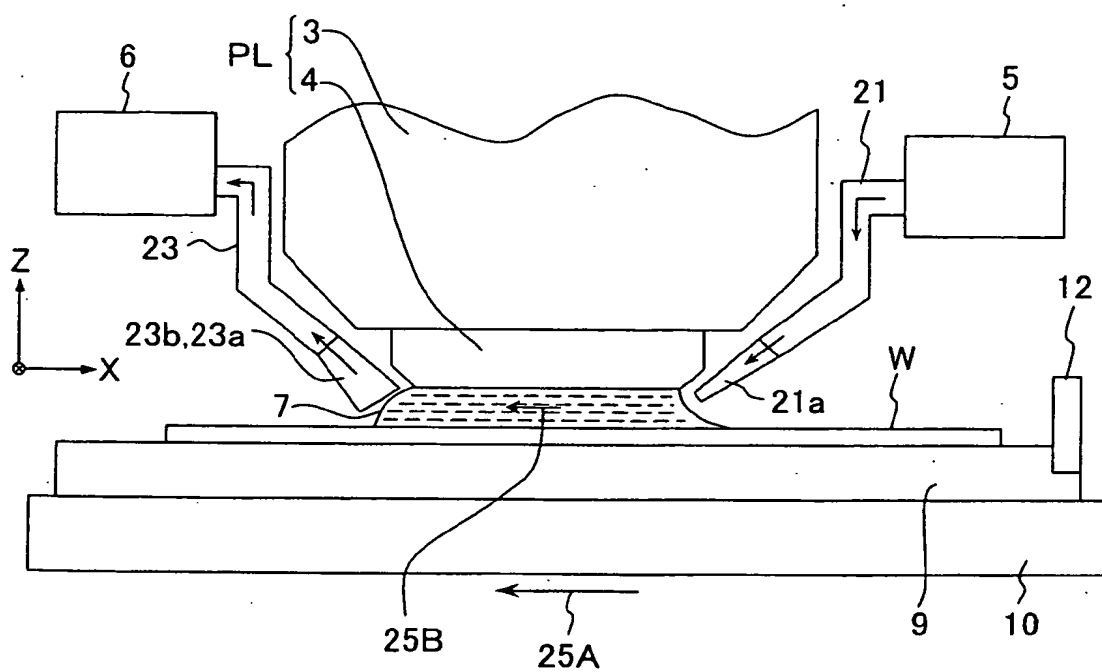


Fig. 5

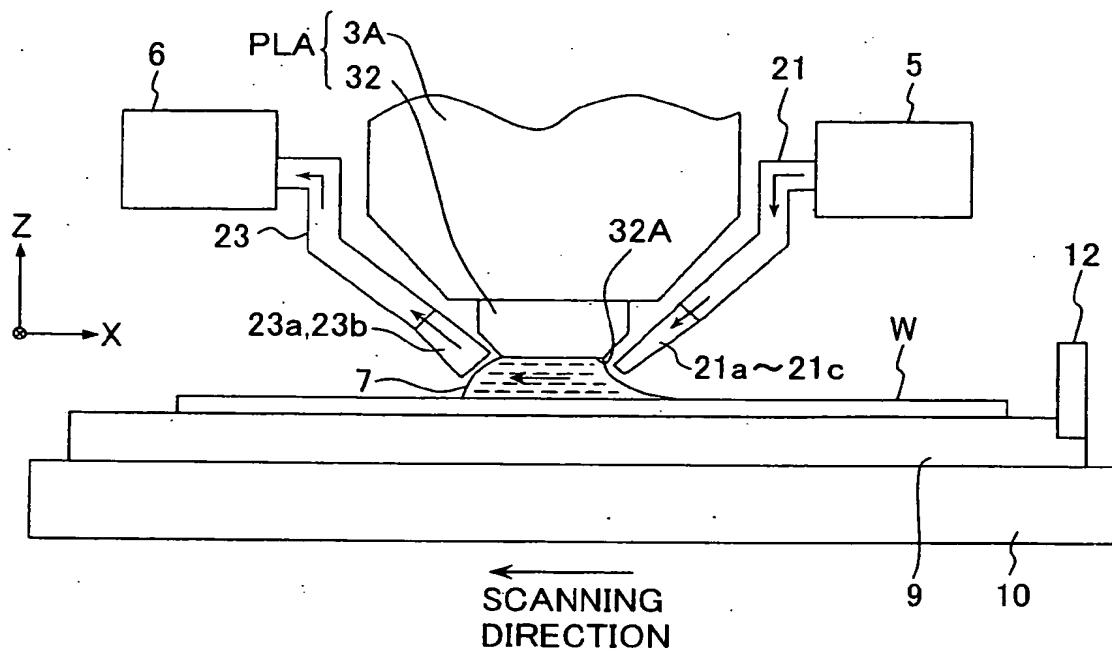


Fig. 6

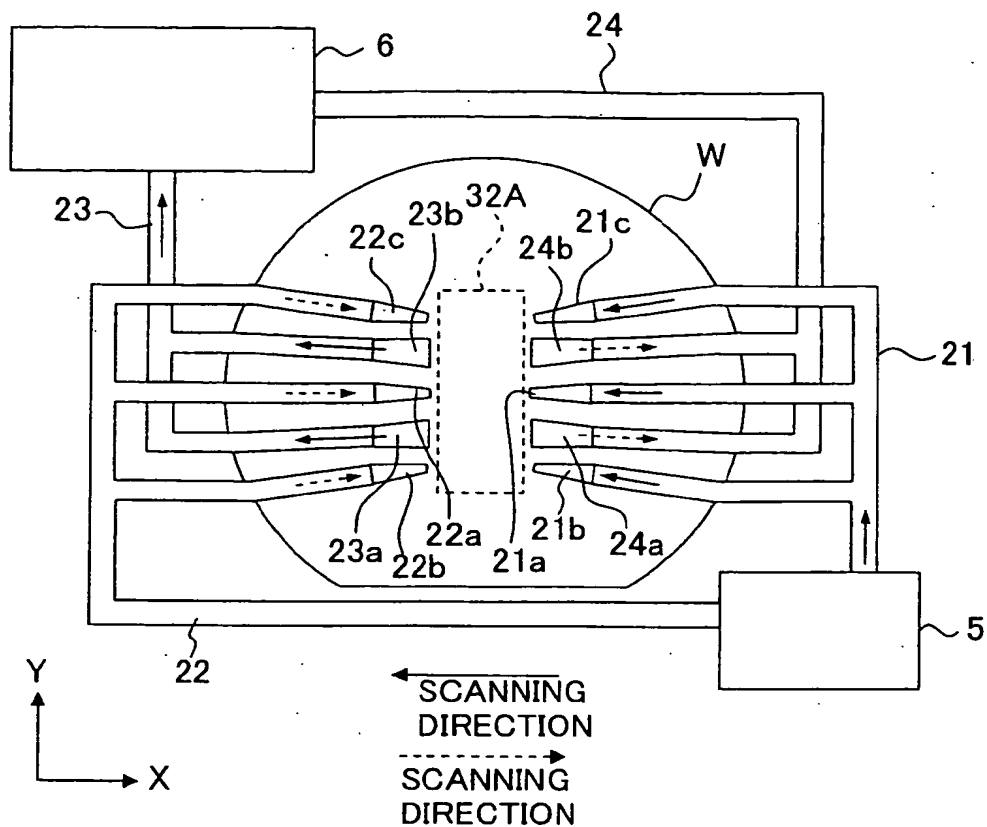


Fig. 7

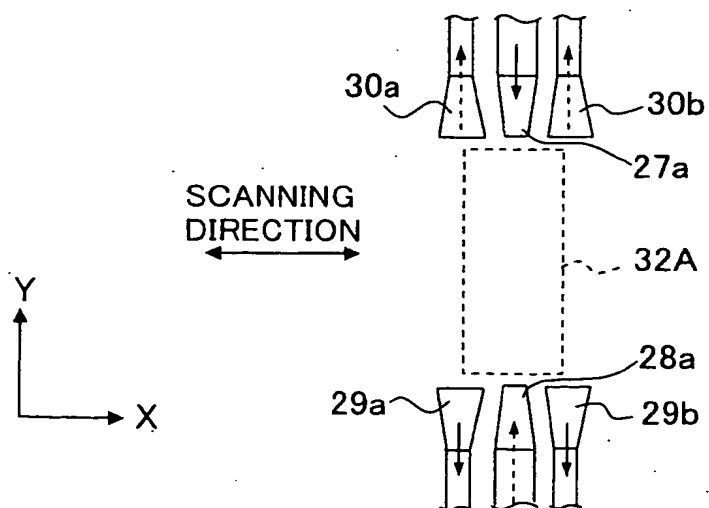


Fig. 8

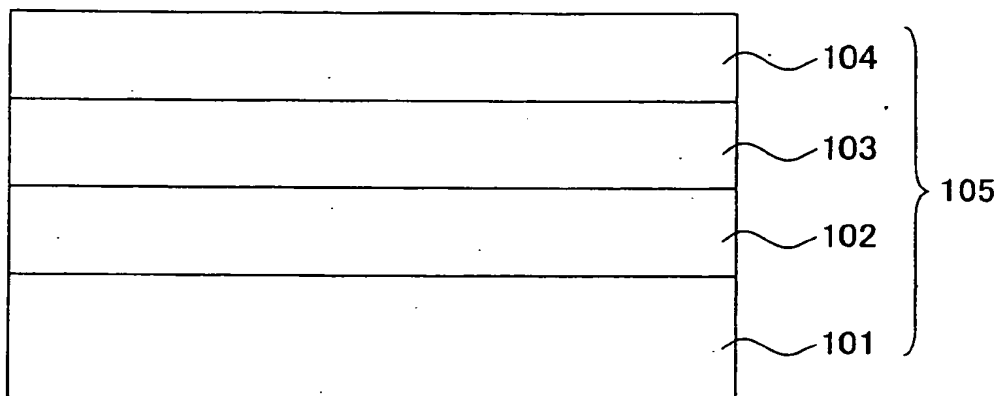




Fig. 9

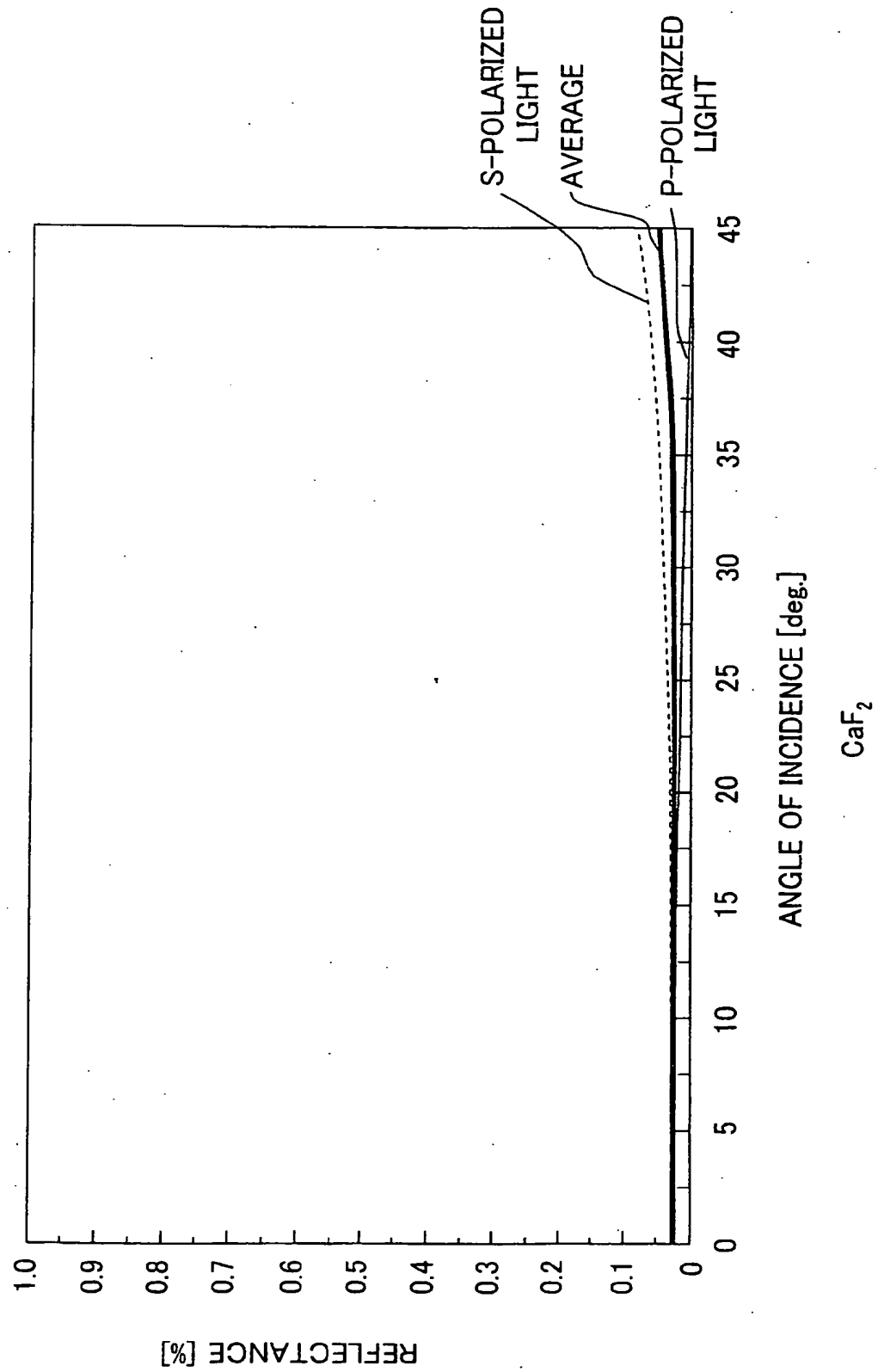
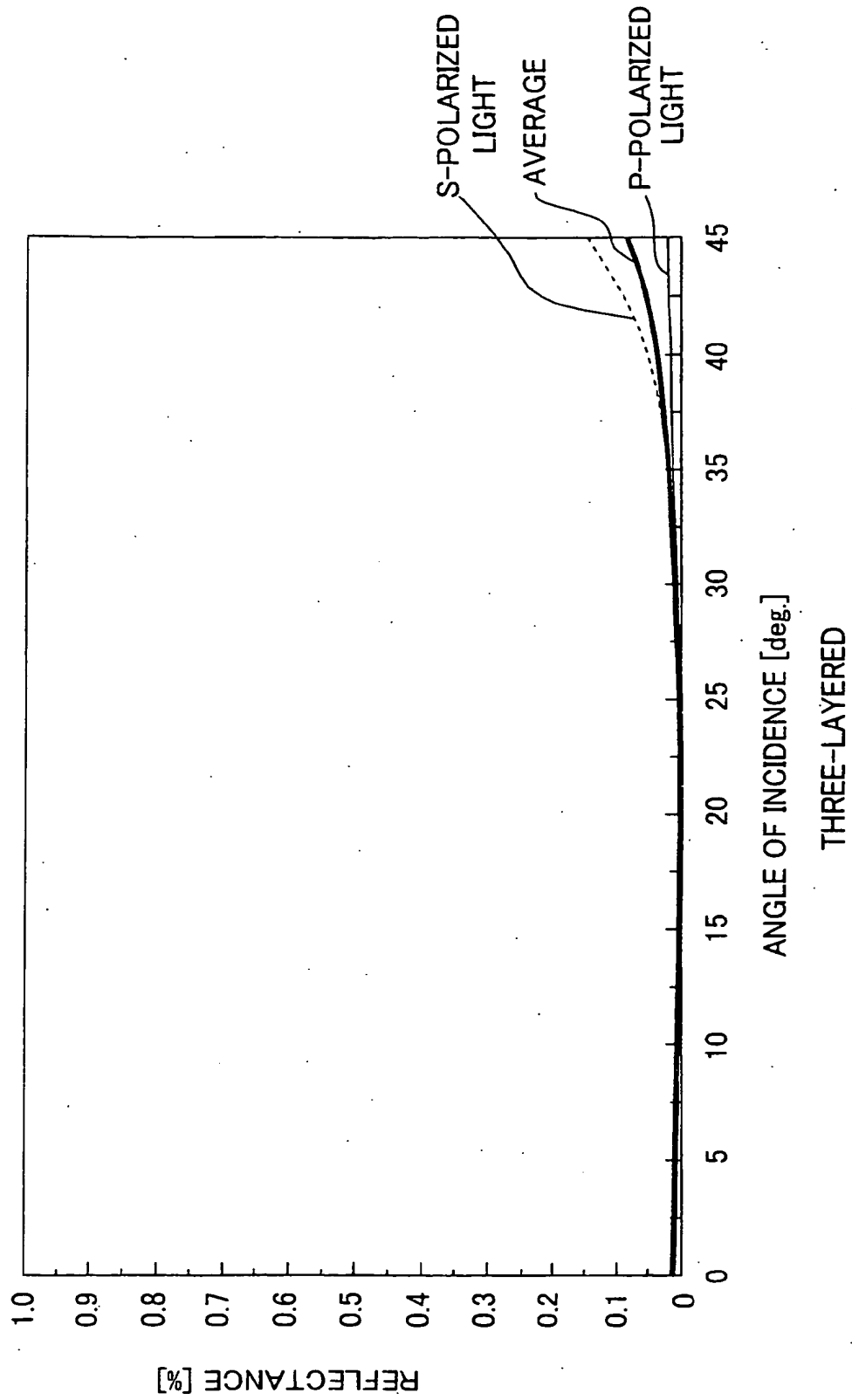


Fig. 10



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/15780

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.<sup>7</sup> H01L21/027, G03F7/20, G02B1/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>7</sup> H01L21/027, G03F7/20, G02B1/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

|                           |           |                            |           |
|---------------------------|-----------|----------------------------|-----------|
| Jitsuyo Shinan Koho       | 1926-1996 | Toroku Jitsuyo Shinan Koho | 1994-2004 |
| Kokai Jitsuyo Shinan Koho | 1971-2004 | Jitsuyo Shinan Toroku Koho | 1996-2004 |

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                        | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | WO 99/49504 A1 (NIKON CORP.),<br>30 September, 1999 (30.09.99),<br>Page 1<br>& AU 99/27479 A                              | 1-13                  |
| A         | EP 834773 A2 (NIKON CORP.),<br>08 April, 1998 (08.04.98),<br>Page 1<br>& JP 10-154659 A & US 5825043 A<br>& KR 98/32589 A | 1-13                  |
| A         | JP 2001-91849 A (Olympus Optical Co., Ltd.),<br>06 April, 2001 (06.04.01),<br>Page 1<br>(Family: none)                    | 1-13                  |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

|                                                                                                                                                                         |                                                                                                                                                                                                                                                  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| * "A" Special categories of cited documents:<br>document defining the general state of the art which is not considered to be of particular relevance                    | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                                              |
| "E" earlier document but published on or after the international filing date                                                                                            | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                                                                     |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "O" document referring to an oral disclosure, use, exhibition or other means                                                                                            | "&" document member of the same patent family                                                                                                                                                                                                    |
| "P" document published prior to the international filing date but later than the priority date claimed                                                                  |                                                                                                                                                                                                                                                  |

Date of the actual completion of the international search  
18 March, 2004 (18.03.04)

Date of mailing of the international search report  
06 April, 2004 (06.04.04)

Name and mailing address of the ISA/  
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/15780

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                             |                       |
|-------------------------------------------------------|---------------------------------------------------------------------------------------------|-----------------------|
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages          | Relevant to claim No. |
| A                                                     | JP 2000-58436 A (NIKON CORP.),<br>25 February, 2000 (25.02.00),<br>Page 1<br>(Family: none) | 1-13                  |

Form PCT/ISA/210 (continuation of second sheet) (July 1998)